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APPLICATION NUMBER: ***60/556,717***
FILING DATE: ***March 25, 2004***
RELATED PCT APPLICATION NUMBER: ***PCT/US05/09977***

Certified by

Jon W. Dudas

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. ER 445940168 US

INVENTOR(S)

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Additional inventors are being named on the ______ *separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

Method of Increasing the Production of Hydrocarbon Liquids and Gases by Reducing or Eliminating Water Block at Well Bores and at the Faces of Hydraulic

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ENCLOSED APPLICATION PARTS *(check all that apply)*

[X] Specification *Number of Pages* 15

[X] Drawing(s) *Number of Sheets* 17

☐ Application Date Sheet. See 37 CFR 1.76

☐ CD(s), Number ______

[X] Other (specify) Attachment A - Disclosure by Inventor 3 Pages

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

[X] Applicant claims small entity status. See 37 CFR 1.27.

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[X] No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: ______

Respectfully submitted,

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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

Method of Increasing the Production of Hydrocarbon Liquids and Gases by Reducing or Eliminating Water Block at Well Bores and at the Faces of Hydraulic Fractures

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The attached document, Attachment A, has been written by the inventors and is hereby incorporated by reference in the current provisional application.

TITLE

Method of Increasing the Production of Hydrocarbon Liquids and Gases by Reducing or Eliminating Water Block at Well Bores and at the Faces of Hydraulic Fractures

TECHNICAL FIELD

The present invention relates to the field of hydrocarbon exploration and extraction. More particularly, the present system discloses a method for removing or eliminating water and/or gas condensates blockage in well bores and at the face of hydraulic fractures by using the wetting and related interfacial properties of various oil forms in order to decrease the forces of capillary retention of water and/or gas condensates and thereby increase the efficiency of extraction of hydrocarbons from underground reservoirs.

REFERENCES

PRIOR ART

Widmyer claimed in his patent (USP2865453)[15] injection of liquid petroleum distillate, of substantially the same viscosity as water, either with or without added surfactant. A gas such as air or flue gas is then injected at sufficient rate and in sufficient volume to drive the water block from the near well bore region for a substantial distance into the adjacent oil or gas formation. A second injection of liquid petroleum distillate is proposed preferably with added surfactant such as N-octodecyl disodium sulfosuccinamate. The surfactant decreases the interfacial tension between water and gas or oil and so aids in additional removal of water from the vicinity of the well bore.

Santourian (USP 3289764) [16] stated that, with proper setting of packers a driving fluid which may be oil or gas can be used to remove water blocks. It is preferred to use a water-

miscible solvent such as ketone, alcohol and so on, together with some other driving fluid, to remove water block in the well bore vicinity of a production formation. In the process, solvent, such as benzene and toluene, and surfactants could be used as well to further mitigate the adverse effect of the water block.

Ross *et al.* (USP 3554288 and 3653442) [7] invented a method of removing water blocks in hydrocarbon producing wells, especially gas producers. A micellar liquid, which consisted of surfactant such as petroleum sulfonate, co-surfactant such as alcohols and so on, and hydrocarbon such as refined fractions of crude oil, and aqueous medium, is used to remove water block from the vicinity of production well bores by solubilization of the water. The term "solubilize" defines substantial sorption or emulsification of the water blockage. It is postulated that this process might also change rock surface wetting to give preferential flow of hydrocarbon.

Masikewich *et al.* (USP 5877126) [17] claimed that addition of alcohols to drilling fluid can mitigate water block or formation damage during drilling of an oil or gas reservoir.

Dewenter *et al.* (USP 6165948) [18] suggested that rock surface could be changed into hydrophobic states by using organosilicon compounds. Dispersion of these compounds can be aided by surfactants. The process protects a gas reservoir from water block, increases gas deliverability, and mitigates salt crystallization impairment caused by evaporation associated with gas production.

Collins *et al.* (USP 6225263) [19] proposed that injection of alkyl ether of polyethylene glycol, with hydrophilic lipophilic balance (HLB) value of 12-17, could be used to reduce water blocking and increase oil and/or gas recovery.

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BACKGROUND

Accumulation of water around a wellbore, commonly described as water block, is widely recognized as a serious cause of decrease in production of hydrocarbon fluids which include both oil and gas and also liquid hydrocarbon condensates. Water blocking can be defined as the consequence of higher water saturation around the near-well-bore formation compared to the connate water saturation associated with rock that is more distant from the wellbore.[1-4]

Water blocking can arise from any one or a combination of the following conditions, drilling, completion, fracturing, work over, or casing leaks.[1-7] Because of the higher water saturation in the rock around the wellbore, the productivity of gas or oil flow is reduced. The presence of high water saturation in the wellbore region greatly increases the transmissibility of water into the well and greatly reduces the transmissibility of oil and/or gas. The effect on

transmissibility is expressed through increased relative permeability to water and reduced relative permeability to gas and/or oil. The local change in transmissivity results in drastic suppression of the ability of oil or gas to flow into the well from the surrounding formation[5].

Even under conditions of flow of both phases or flow of hydrocarbon gas and/or oil, high water saturation is maintained around the well bore because of capillary forces. The problem becomes increasingly serious with decrease in permeability of a formation because pore sizes are smaller and capillary action is stronger.[8-9]

The problem of water blocking is further accentuated if the well bore region has been subject to clay particle invasion or clay swelling. Dispersion, migration, and plugging by fine particles during well drilling and completion operations results in smaller pore sizes around the well bore.[4] The locally decreased pore sizes result in impaired permeability[6, 8, 10] and exacerbate the problem of water block by capillary retention. Damaged zones are prevalent in the perforation regions where access to the formation through well casing has been established by means of explosive shaped charges which crush the rock.[11] Crushing of the rock in the local region of the perforation results in reduced pore size with attendant reduced permeability and increased capillary retention of water.

The clean-up or removal of water blocking is currently difficult, expensive, and time-consuming[1, 12]. One approach to mitigating this problem is to treat the well bore with chemicals that adsorb onto the rock surface to render it near neutral to oil wet. Capillary retention forces are reduced and permeability to hydrocarbon is increased. The chemicals proposed for wettability alteration are expensive. Furthermore they may only be effective for a limited time because they are generally held as a monolayer at the rock surface and the wettability alteration may not be stable over time at the prevailing flow conditions.

Some kind of chemicals can be used to enhance the cleanup of the water block. Mcleod *et al.*[8-9] used alcohol to mitigate water blocking of gas production. Kamath *et al.*[1] and Laroche *et al.*[12] studied the effect of various liquids such as brine, alcohols, and toluene on the gas deliverability. They concluded that the cleanup of water block near a well bore

could be divided into two stages. The first stage was fluid displacement which bypassed water and left high retained water saturation around the well bore. This stage lasted about 2 days. The second stage was reduction of water saturation by evaporation driven by gas flow (mass transfer of water into the gas phase as the gas expands during flow into the well bore). The second stage could last for several months. They pointed out that the addition of volatile solvent helped the remediation in the second stage and reduced the duration of the cleanup.

Mahadevan and Sharma[13] reported that the addition of methanol could speed the cleanup of water blocking. Wettability change from water wet to oil wet through using 1% v/v solution of octyldecyltrichlorosilane (OTS) could also aid in the clean up of water blocking in limestone when methanol was used to displace the water block. They mentioned that surfactants which change wettability might be used to enhance clean up of water blocks in tight gas sands.

However, Abrams and Vinegar[14] concluded that if the drawdown pressure was much higher than the capillary pressure of the near-well bore formation, the water block would be removed. Under these conditions there was not much benefit to well treatment with alcohol or alcohol/surfactant to remove water block.

Penny, *et al.*[10] concluded that change in wettability of the rock surface from water wet to oil wet would promote mitigation of water blocks because the capillary pressure and hence capillary retention of water was reduced. In their work, non-emulsifiers (surfactants) dissolved in methanol were employed to induce wetting change from water-wet to non-wet (contact angle ~90°).

Metheven[6] claimed that oil-based mud filtrate, which contained asphalt that was soluble in crude oil or aromatic solvent, significantly increased gas well deliverability and oil or condensate productivity compared to water-based fluids.

SUMMARY OF THE INVENTION

In one of many possible embodiments, the present invention provides a method for reducing or eliminating water block by removing the water from around a well bore, injecting crude oil, surface precipitation of asphaltenes in the well bore region by injecting aliphatic hydrocarbons or other hydrocarbon fluids of low solvency for asphaltenes, decreasing the wettability to water of mineral surfaces within the water block and well bore to near neutral to oil wet by removing the water, injecting crude oil, and surface precipitation of asphaltenes thereby decreasing capillary retention forces of water, or water and/or condensates from gases and increasing the flow of hydrocarbon liquids or gases from the reservoir.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

A new approach to mitigation of water block: wettability alteration by adsorption from crude oil and by surface precipitation of asphaltenes.

In laboratory studies, Xie and Morrow[20] showed that when the wettability of a rock was altered by adsorption from crude oil, the initial water content of the rock at the time of adsorption had a dominant effect on the reduction in capillary forces as determined by measurement of rate and extent of spontaneous imbibition. The lower the initial water saturation, the greater the reduction in water-wetness of the rock surface. Tong *et al.*[21-22] showed that the wettability induced by the adsorption of organic film from asphaltic crude oils in the presence of connate water was stable to many cycles of exposure to oil and water.

Furthermore the water saturation in the rock could be readily reduced by flow of oil after the first cycle of treatment, so that low water saturations, a key factor in reduction of wettability to water, would pertain if the rock is re-exposed to crude oil. Tie *et al.*[23] showed that the extent of wettability alteration depended on how crude oil was displaced from the rock by some other oleic phase.

Direct displacement of crude oil by a hydrocarbon with low solvency for the asphaltenes in crude oil resulted in the most pronounced wettability change for both sandstone and carbonate rocks without significant reduction in permeability. The low solvency hydrocarbon typically has significantly lower refractive index than the crude oil. The low solvency hydrocarbon and hydrocarbon gas will hereafter be referred to as aliphatic mineral oil (or more briefly as mineral oil-carbon chain number equal to and greater than about 5) and gas (carbon chain number less than about 5). The change in wettability is ascribed principally to the surface precipitation of asphaltenes from the crude oil, a wettability alteration mechanism first described by Buckley and co-workers (see for example Al-Maamari and Buckley, 2003)[24]. Surface precipitation results from incompatibility of the crude oil and the mineral oil with respect to the solvency of asphaltenes contained in the crude oil.

Comparable incompatibility and deposition of asphaltenes can result from exposure of crude oil to hydrocarbon gas or gas condensate. It is common engineering practice to avoid the precipitation of asphaltenes because it is well-known that they can cause formation damage. However, according to the hydrocarbon production scenario wettability alteration by adsorption and/or surface precipitation from crude oil can be effected by injection of crude oil with essentially no damage to the formation. Greater wettability alteration by surface precipitation can be effected by following injection of an oleic or gas phase which induces asphaltene precipitation from the crude oil. Alternatively the gas or gas condensate of the reservoir can facilitate the surface precipitation of asphaltenes.

The lower the water content at the time of treatment, the more effective is the change in wettability. Water saturation could be lowered by injection of a viscous crude oil to increase the effectiveness of wettability alteration by adsorption from the crude oil or by surface precipitation as already described. Different procedures can be employed to reduce high water saturation in the vicinity of a well bore. Enough liquid should be injected so that the distance from the well bore would usually be in the range of about 2 to about 10 feet from the well bore but is not necessarily restricted to this range.

The first method (see Fig. 1) is direct injection of the crude oil followed by a slug of

alkane (usually a mineral oil) to induce wettability alteration towards near neutral to oil wet by surface precipitation from crude oil (see Fig. 1 for the steps in removal of water block and restoration of oil production). If additional removal of water is needed the treatment cycle can be repeated. It has been observed that after adsorption from crude oil the water saturation is more readily decreased.[22] An estimate of observed relationships between treatment cycle and water saturation is presented in Fig. 2.

Large decrease in water saturation around the well bore can be achieved by pre-injection of a slug of a co-solvent of water followed by crude oil (see Fig. 3). After that, a slug of mineral oil (see Fig. 3d) is used to induce wettability alteration. The co-solvent of water can be a water soluble alcohol (e.g. methanol), or an alcohol that is conditionally miscible with both oil and water such as iso-propanol or butanol.

Accumulation of condensate at the well bore is a serious problem in many gas condensate reservoirs. In many instances, accumulation of water around the well bore will also contribute to the local severe reduction in gas permeability. Combinations of water, gas, and condensate lenses to give blockage by a form capillary resistance known as the Jamin effect would be particularly adverse to production. The retention of water could be mitigated by the treatments described below by which water saturation is reduced and the region around the well bore is rendered near neutral to gas condensate wet.

A simple approach to reduction of water block for gas or gas condensate reservoirs by injection of crude oil is shown in Fig. 4. Surface precipitation of crude oil is induced by production of gas (or gas plus condensate).

More effective removal of water can be achieved by injection of a co-solvent of water prior to injection of crude oil (see Fig. 5). Production of gas (or gas plus condensate) is used to induce surface precipitation from the crude oil as illustrated in Fig. 5d and to remove water and crude oil from the well bore region so that well productivity is increased (see Fig. 5e).

In a third approach to removal of water block in gas and gas condensate wells shown

in Fig. 6, the first three steps are the same as 5a, 5b, and 5c, but then surface precipitation is induced by injection of mineral oil (Fig. 6c). The liquids used to induce wettability change are then pumped off or forced from the well bore region by gas production.

Another form of water block is commonly referred to as coning. Coning arises because the hydrocarbon zone overlies an aquifer as illustrated in Fig. 7. The proposed treatments for oil, gas, and gas condensate reservoirs can be used in accordance with the nature of the hydrocarbon zone to increase the permeability of hydrocarbon relative to water around the well bore and so give a higher ratio of hydrocarbon to brine production.

In some cases, very low concentration of surfactants such as amine can be added in the crude oil or alcohols to aid wettability change towards decreased water wetness. In all examples of wettability alteration, when a well is produced, the water block does not re-form because the induced wettability change greatly reduces the forces of capillary retention which act around the well bore. Jadhunandan and Morrow[25] pointed out that oil recovery by water flooding was maximized at very weakly water-wet conditions. In addition, change in the rock surface wettability towards near neutral wet conditions enhances relative permeability with respect to multiphase flow including the possibility of simultaneous flows of gas, oil and brine.

Water block is also a serious problem with respect to production from hydraulically fractured wells. The fracture is basically an enlargement of the drainage region of the well bore (see Fig. 8). Fracture faces are commonly blocked either by invasion of water associated with the fracturing procedure or by formation water. The procedures based on wettability alteration by adsorption and/or surface precipitation from crude oil described above to remove water block from around a well bore also apply to mitigation of water blocks at fracture faces. Additionally the crude oil can be used as the propant liquid followed by a surface precipitant (usually mineral oil) prior to clean up.

Based on these observations, it is claimed that reduction of water saturation followed by treatment of rock through adsorption and/or surface precipitation from crude oil which

may be coupled with injection of chemicals, such as alkanes, or production of natural gas, to induce surface precipitation of asphaltenes, is a low cost method of reducing or eliminating water block at well bores.

In summary, the specifically described method claims that the local water saturation can be reduced by injection of crude oil and by multiple injections of crude oil - for more effective wettability alteration. Injection of a co-solvent can also be used to reduce water saturation prior to exposure to crude oil. Robust wettability alteration by surface precipitation from crude oil can be induced by displacing the crude oil with aliphatic mineral oil or by exposing the crude oil to reservoir natural gas or gas plus condensate through production. A mutually soluble hydrocarbon to oil and water, such as a longer hydrocarbon chain alcohol such as butanol, can also serve as a precipitant.

The wettability may range from very weakly water wet through neutral to oil wet as indicated by spontaneous imbibition of either brine or oil. The described treatments for improved hydrocarbon liquid and gas productivity have application to perforated regions, open holes, and to the faces of hydraulic fractures.

The preceding description has been presented only to illustrate and describe embodiments of invention. It is not intended to be exhaustive or to limit the invention to any precise form disclosed. Many modifications and variations are possible in light of the above teaching.

The foregoing embodiments were chosen and described in order to illustrate principles of the invention and some practical applications. The preceding description enables others skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the following claims.

WHAT IS CLAIMED IS:

1. A method for reducing or eliminating water block comprising;

removing the water from around a well bore of a hydrocarbon reservoir;

injecting crude oil with added low concentrations of an oil soluble surfactant to enhance wettability alteration in the well bore region;

precipitating surface precipitants of asphaltenes in the well bore region by injecting aliphatic hydrocarbons or other precipitant means thereby decreasing forces of capillary retention for water and/or gas condensates allowing an increasing flow of hydrocarbon fluids from the hydrocarbon reservoir.

2. The method of claim 1, removing the water further comprising injecting co-solvent for brine.

3. The method of claim 2, further comprising injecting the brine co-solvent to a range of between 2 and 10 feet from the well bore.

4. The method of claim 2, wherein the brine co-solvent is such as one of the following alcohols: methanol, ethanol, iso-proponol, butanol.

5. The method of claim 2, wherein the brine co-solvent is a micellar surfactant solution of an alcohol or other co-solvent.

6. The method of claim 1, wherein the crude oil used for injecting is selected for its known wettability alteration properties including surface precipitation to the mineral materials in the well bore region.

7. The method of claim 1, further comprising allowing any of the gas or hydrocarbon condensates of a gas reservoir to interact with the crude oil to cause surface precipitation of asphaltenes in the well bore region.

8. The method of claim 1, further comprising repeating the removing of water by injecting crude oil multiple times in order to maintain altered wettability of the well bore region and to reduce water saturation in the well bore region.

9. The method of claim 1, wherein the aliphatic hydrocarbon comprises predominantly aliphatic refined mineral oil.

10. The method of claim 1, further wherein the hydrocarbons are natural gases.

11. The method of claim 1, wherein the method of reducing water block is used in the well bore region, including perforated regions, open holes, and faces of hydraulic fractures.

12. The method of claim 1, wherein the changing the wettability is to a weakly water wet form.

13. The method of claim 1, wherein the changing the wettability is to a neutral wet form.

14. The method of claim 1, wherein the changing the wettability to an oil wet form.

15. The method of claim 1, wherein the changing the wettability further comprises degrees of wetting between weakly water wet and oil wet.

16. The method of claim 1, wherein the changing the wettability is promoted by addition of a low concentration of an oil soluble surfactant.

17. The method of claim 1, wherein the oil soluble surfactant is an amine.

18. A method for reducing or eliminating water block comprising;

decreasing the water wetness of mineral surfaces in the well bore region by removing the water;

injecting crude oil, and surface precipitation of asphaltenes thereby decreasing forces of capillary retention for water and/or gas condensates allowing an increasing flow of hydrocarbon fluids from the hydrocarbon reservoir.

19. All inventions as herein disclosed.

Fig. 1 Method 1 of treatment for oil reservoir case

Fig.1a

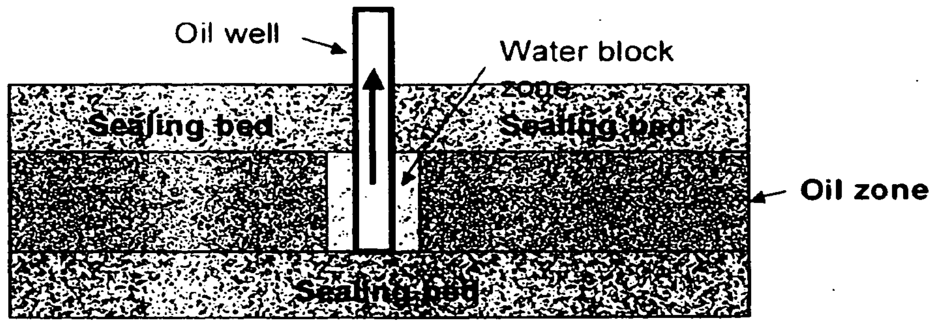
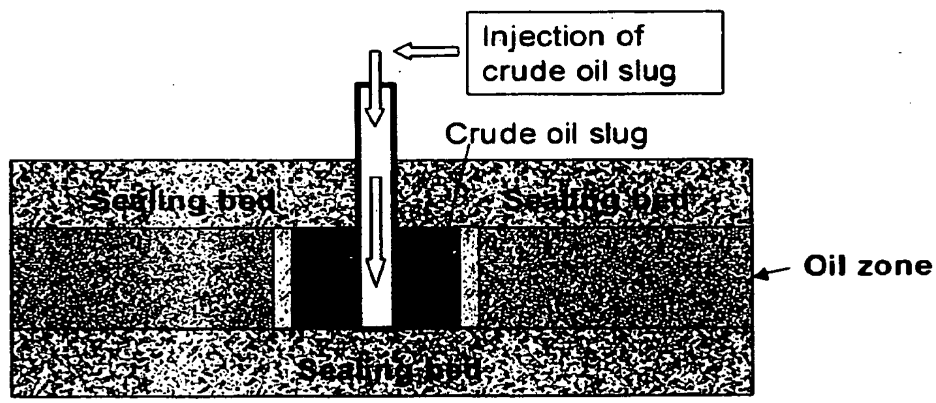


Fig.1b



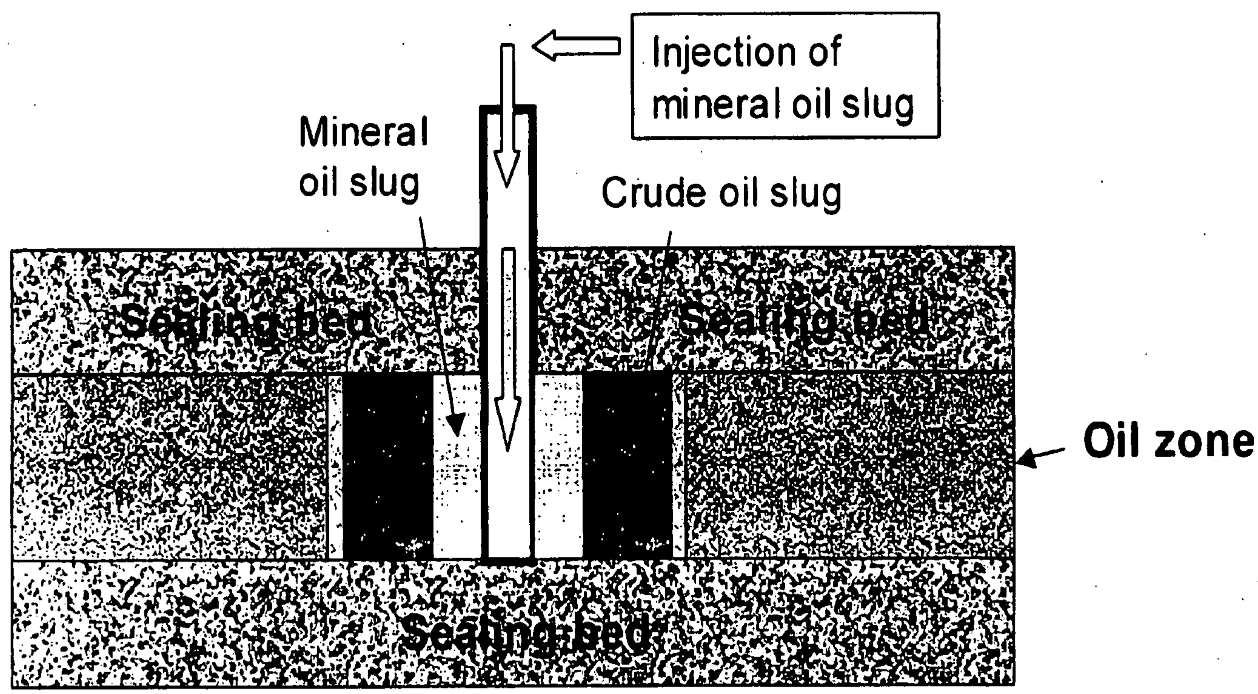

Injection of
mineral oil slug
Mineral
oil slug
Crude oil slug
Sealing bed
Sealing bed
Oil zone
Sealing bed

Fig.1c

Fig. 1d

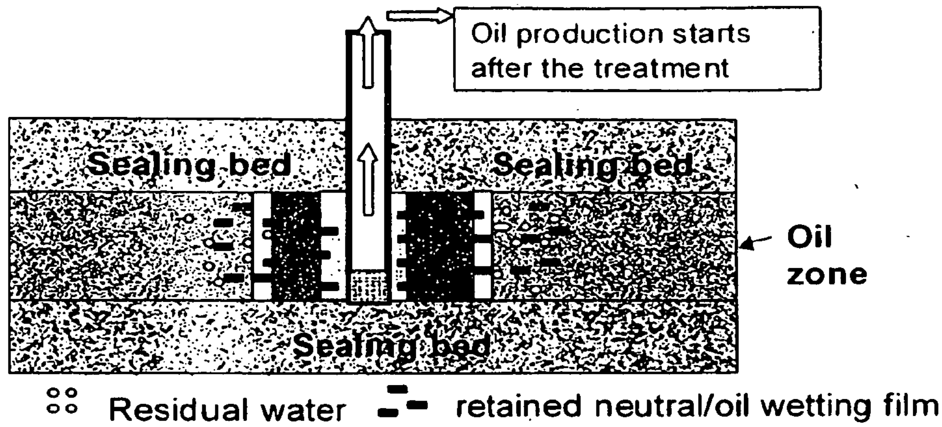

Oil production starts after the treatment
Sealing bed
Sealing bed
Oil zone
Sealing bed
Residual water
retained neutral/oil wetting film

Fig. 1e

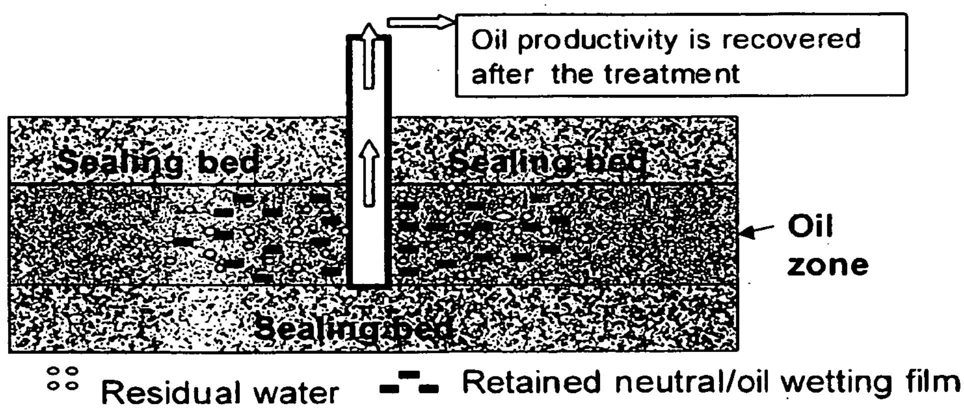

Oil productivity is recovered after the treatment
Sealing bed
Sealing bed
Oil zone
Sealing bed
Residual water
Retained neutral/oil wetting film

Fig. 2 The sketch of water saturation change near well bore vs. cycle numbers of treatment

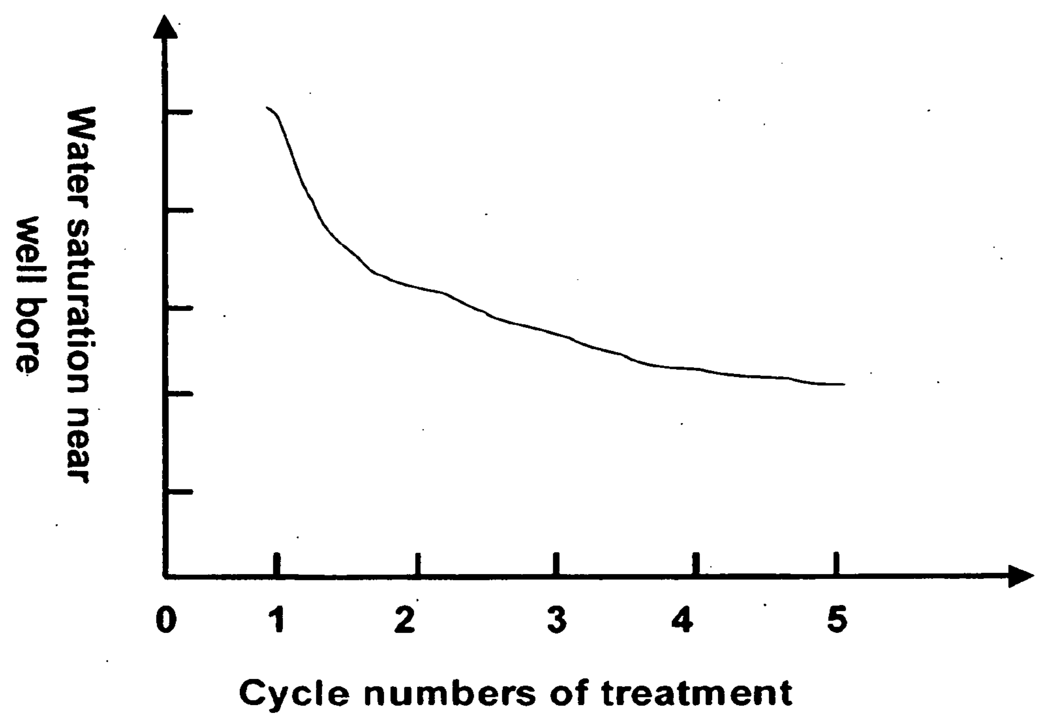


Fig. 3 Method 2 of treatment for oil reservoir case

Fig.3a

Fig.3b

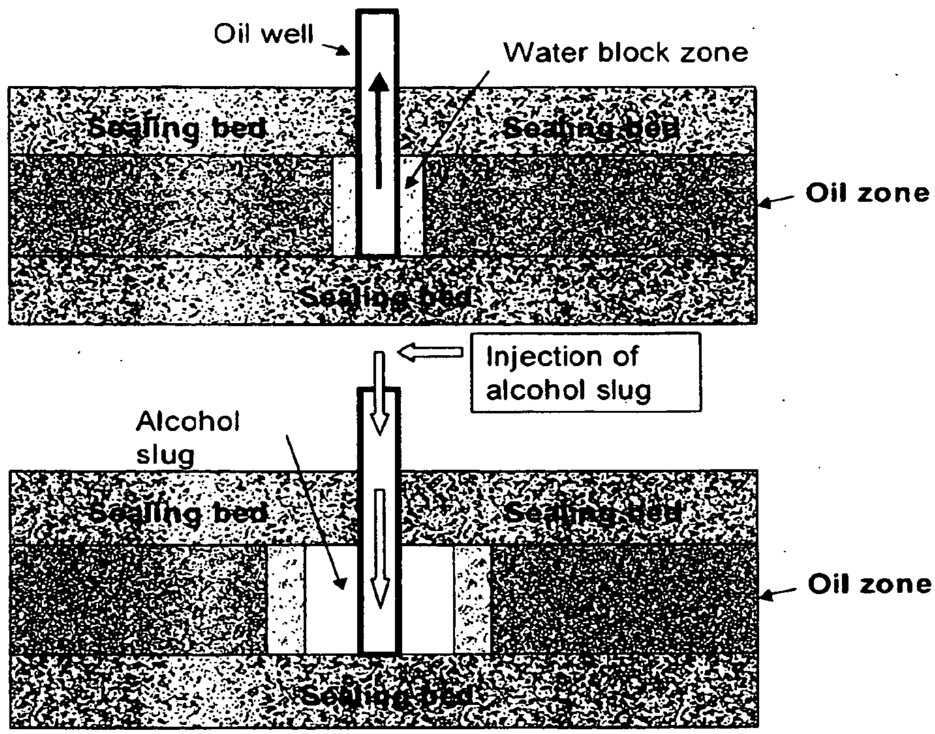


Fig.3c

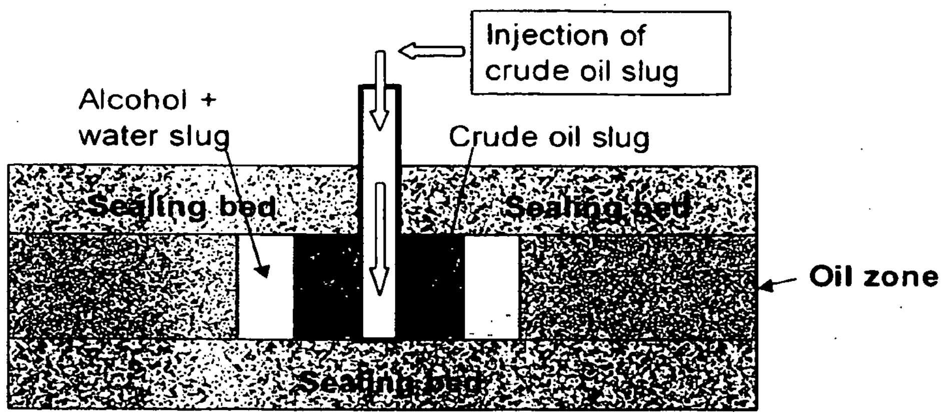

Injection of crude oil slug
Alcohol + water slug
Crude oil slug
Sealing bed
Sealing bed
Oil zone
Sealing bed

Fig.3d

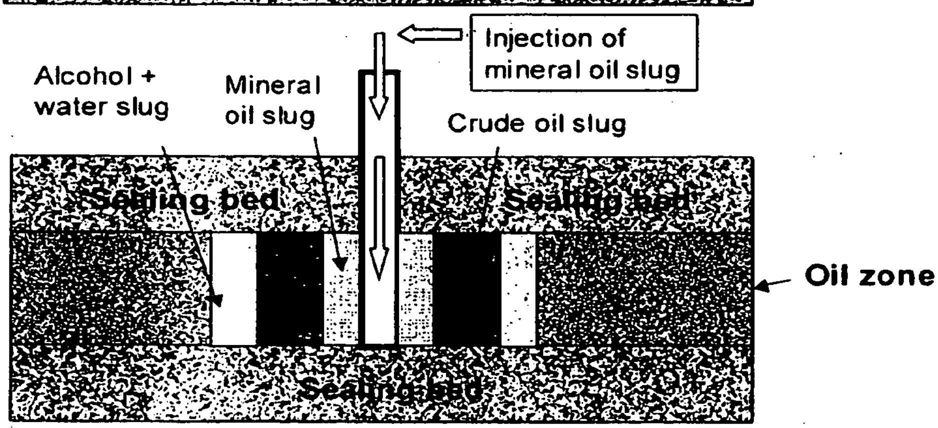

Injection of mineral oil slug
Alcohol + water slug
Mineral oil slug
Crude oil slug
Sealing bed
Sealing bed
Oil zone
Sealing bed

Fig.3e

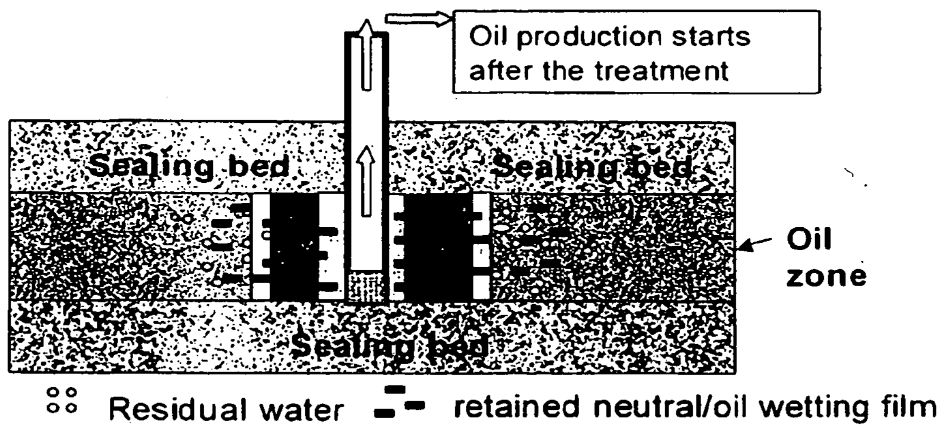

Oil production starts after the treatment
Sealing bed
Sealing bed
Oil zone
Sealing bed
Residual water
retained neutral/oil wetting film

Fig.3f

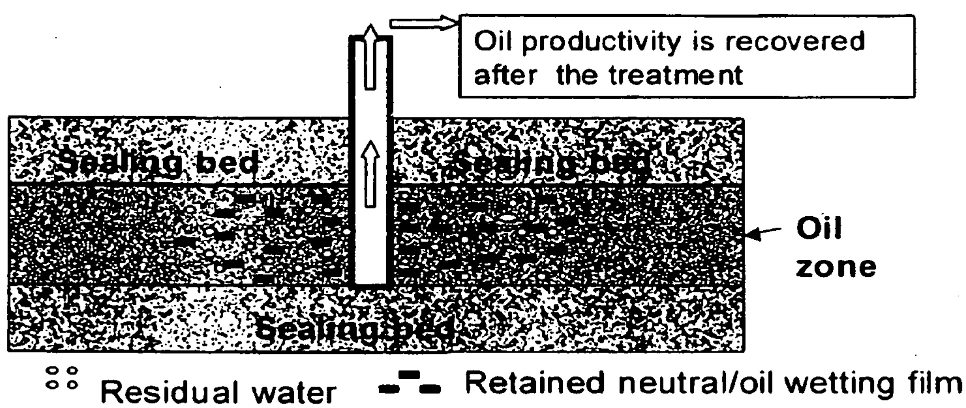

Oil productivity is recovered after the treatment
Sealing bed
Sealing bed
Oil zone
Sealing bed
Residual water
Retained neutral/oil wetting film

Fig. 4 Method 1 of treatment for gas or gas condensate reservoir case

Fig.4a

Fig.4b

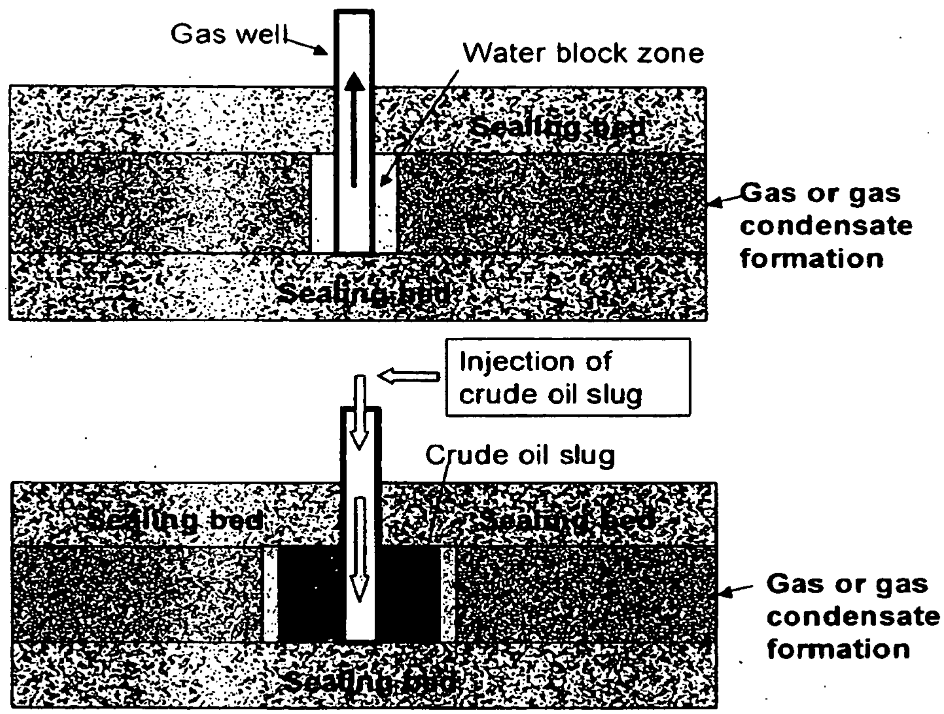
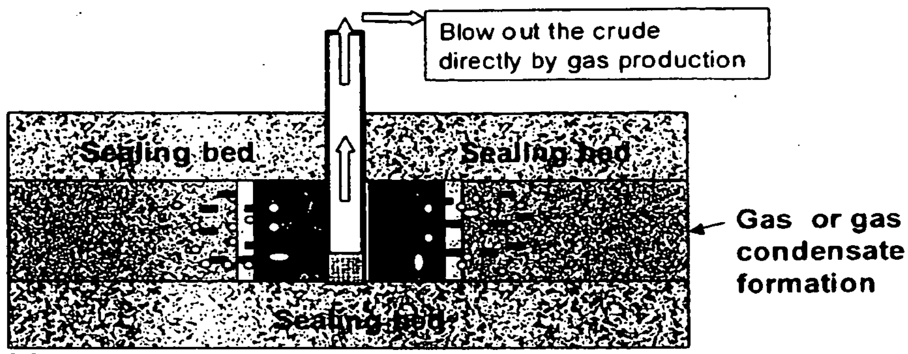
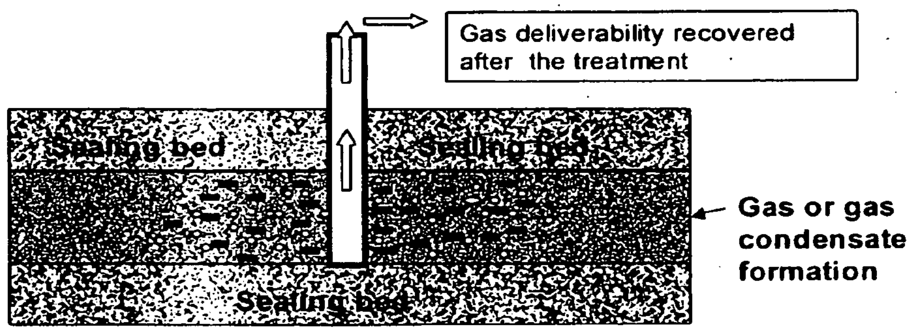


Fig.4c



Residual water Retained neutral/oil wetting film

Fig. 4d



Residual water Retained neutral/oil wetting film .

Fig. 5 Method 2 of treatment for gas or gas condensate reservoir case

Fig.5a

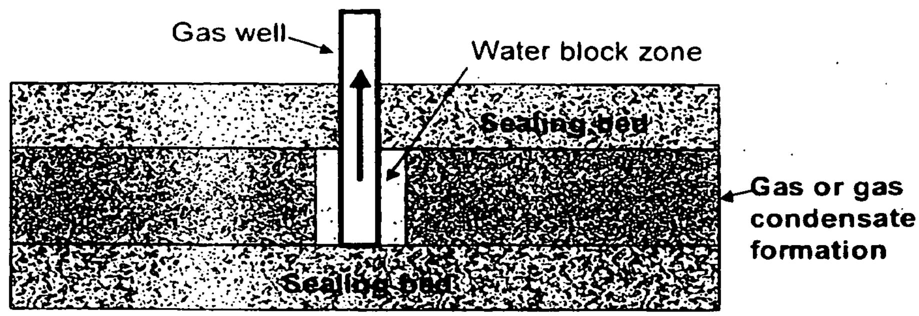


Fig.5b

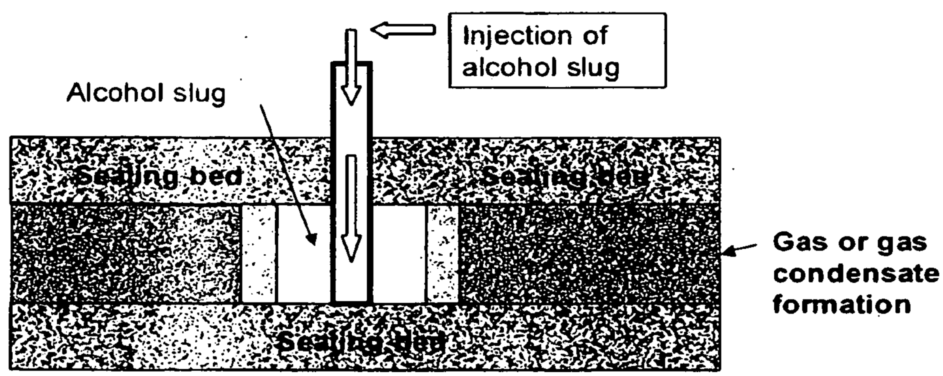


Fig.5c

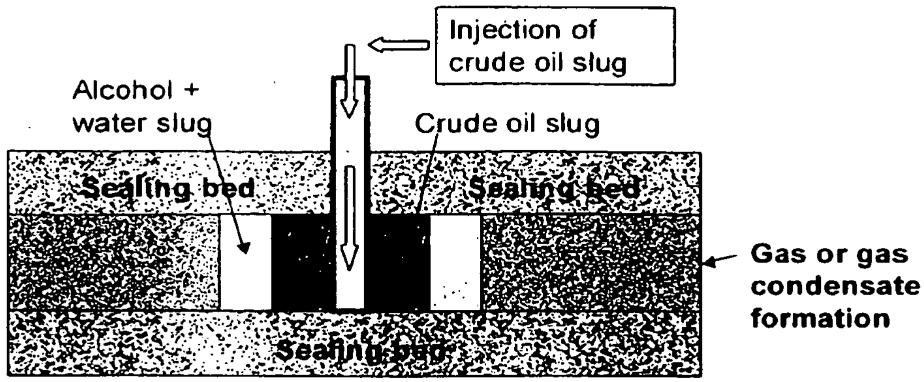

Injection of
crude oil slug
Alcohol +
water slug
Crude oil slug
Sealing bed
Sealing bed
Sealing bed
Gas or gas
condensate
formation

Fig.5d

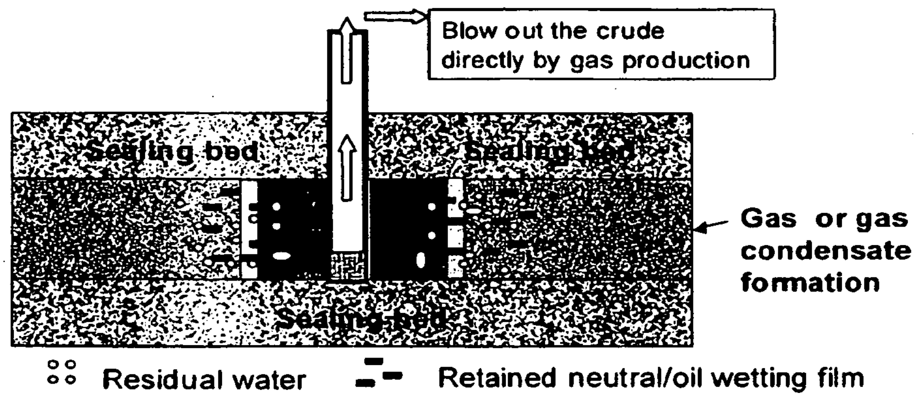

Blow out the crude
directly by gas production
Sealing bed
Sealing bed
Sealing bed
Gas or gas
condensate
formation
Residual water
Retained neutral/oil wetting film

Fig. 5e

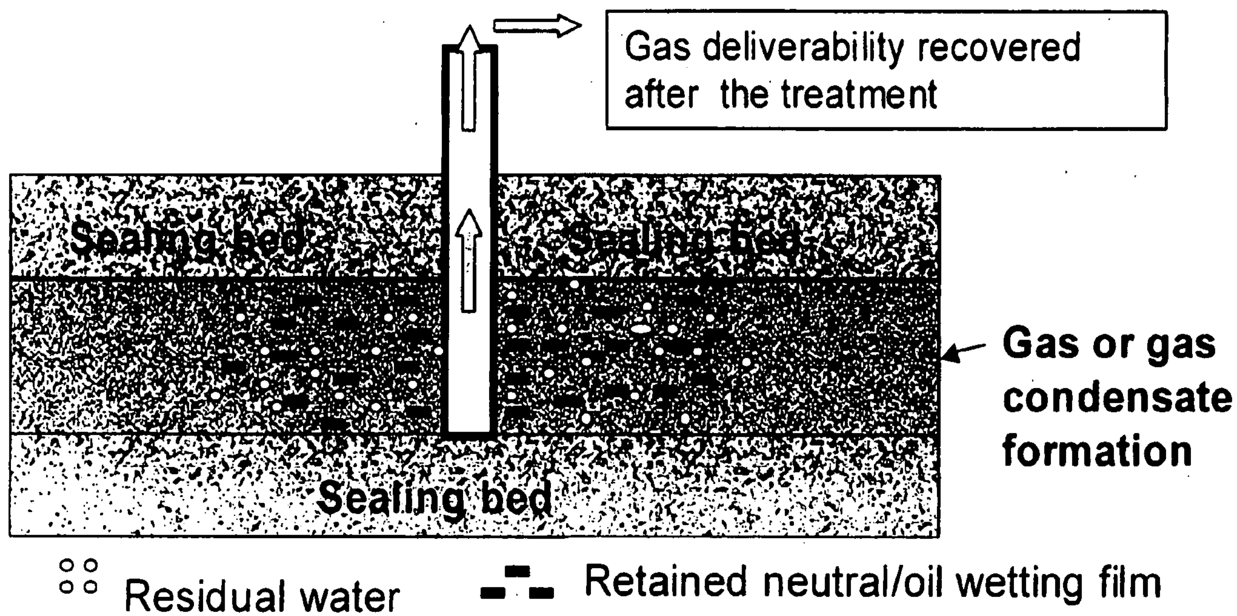

Gas deliverability recovered after the treatment
Sealing bed
Sealing bed
Sealing bed
Gas or gas condensate formation
Residual water
Retained neutral/oil wetting film

Fig. 6 Method 3 of treatment for gas or gas condensate reservoir case

Fig.6a

Fig.6b

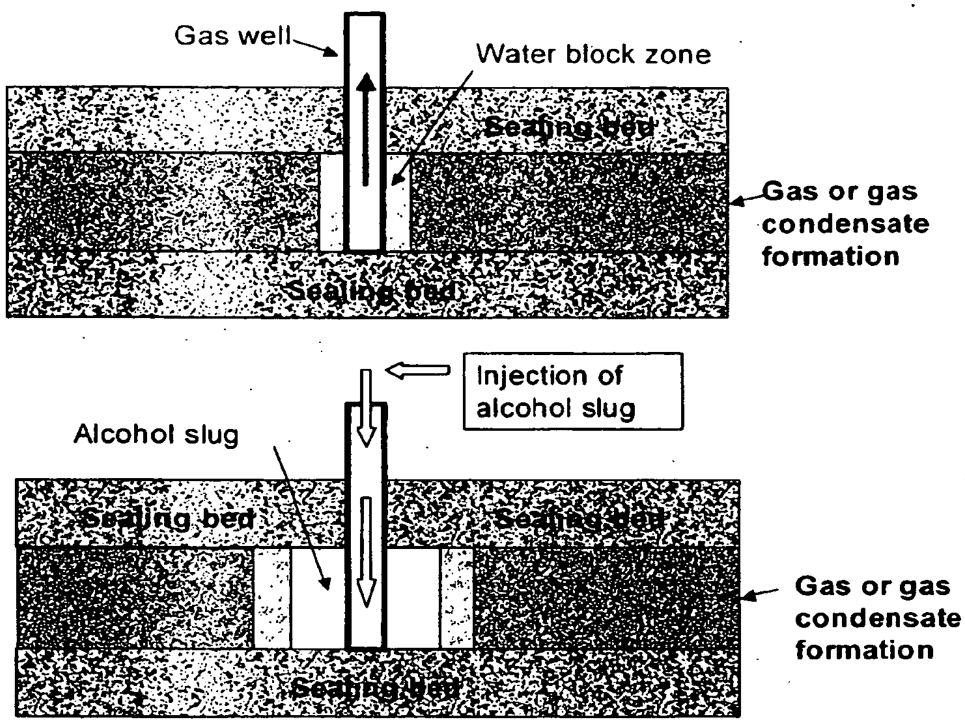


Fig. 6c

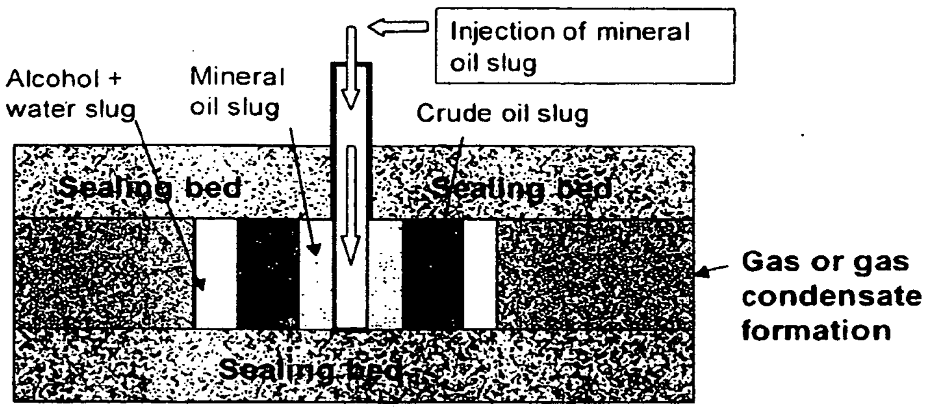

Injection of mineral oil slug
Alcohol + water slug
Mineral oil slug
Crude oil slug
Sealing bed
Sealing bed
Sealing bed
Gas or gas condensate formation

Fig. 6d

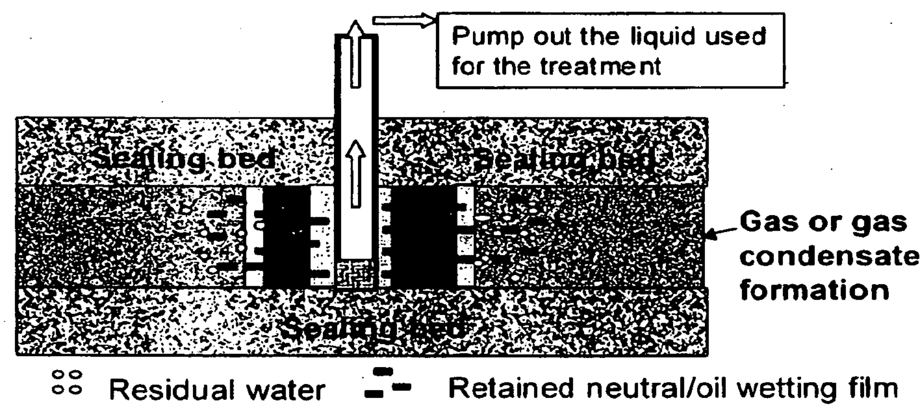
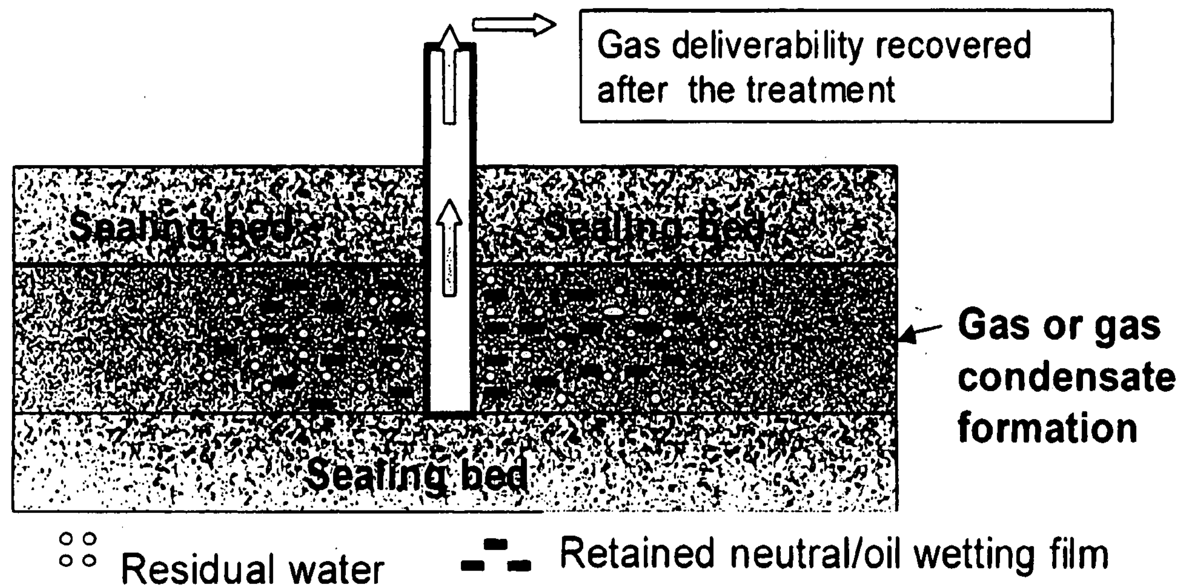

Pump out the liquid used for the treatment
Sealing bed
Sealing bed
Sealing bed
Gas or gas condensate formation
Residual water
Retained neutral/oil wetting film

Fig. 6e



Gas deliverability recovered after the treatment
Sealing bed
Sealing bed
Gas or gas condensate formation
Sealing bed
Residual water
Retained neutral/oil wetting film

Fig. 7 Water coning case

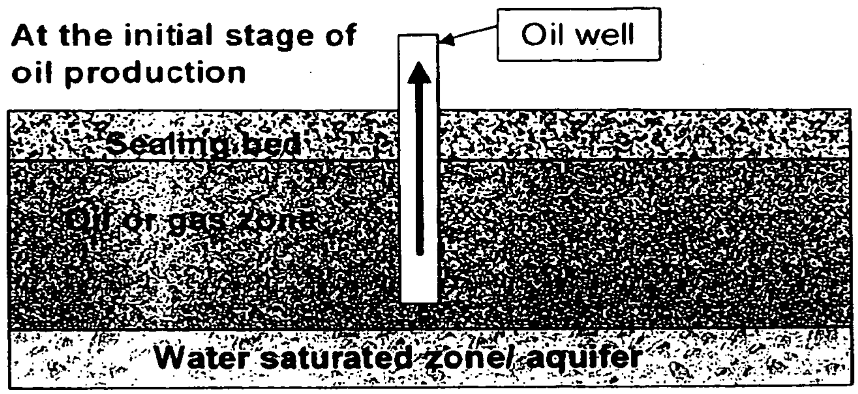


Fig. 7a

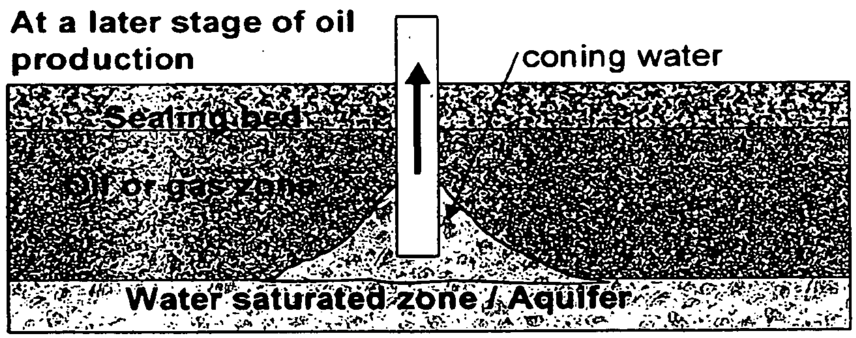


Fig. 7b

Fig. 8 Case with hydraulic fracture wells—plane view sketch